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Synthesis and Properties of Tricarbonyl(*exo*-cyclopentadienyl-η^5-cyclohexadienyl)manganese

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Tricarbonyl(*exo*-cyclopentadienyl-η^5-cyclohexadienyl)manganese (**2**) has been prepared by the reaction of $(C_6H_6)Mn(CO)_3^+$ cation with NaCp. **2** reacts with *n*-BuLi to produce a lithiated compound, presumably $[Li][(exo\text{-}C_5H_4\text{-}\eta^5\text{-}C_6H_6)Mn(CO)_3]$ (**3**), which reacts with $M(CO)_5Br$ (M = Mn, Re), $M(CO)_3(CH_3CN)_3$ (M = Cr, Mo, W), and $FeCl_3$ to yield the corresponding organometallic compounds. The molecular structure of $(CH_3)(CO)_3W[\eta^5\text{-}C_5H_4\text{-}\{(\eta^5\text{-}C_6H_6)Mn(CO)_3\}]$ (**5c**) (space group $P2_1/n$; unit cell parameters a = 7.954 (1) Å, b = 21.932 (3) Å, c = 10.509 (1) Å, β = 96.40 (1)°, and V = 1822.0 (5) Å^3; R = 2.42%, R_w = 2.81%) has been determined.

Introduction

Whereas the utilities of cyclopentadienyl or cyclohexadiene ligands are well-known in organometallic chemistry, ligands which incorporate both a cyclohexadienyl and a cyclopentadienyl ligand have received comparatively little attention. Ligands of this type could be utilized in the formation of bimetallic compounds, which in turn might prove useful in probing chemical reactions between two different metal centers which are not directly bonded to each other.[1] Chemical processes involving two or more organometallic units in combination with one another are becoming of increasing importance.

In connection with our current research program concerning cyclohexadienylmetal compounds,[2] we have found that the cyclopentadiene moiety of tricarbonyl(*exo*-cyclopentadienyl-η^5-cyclohexadienyl)manganese (**2**) could be used as a π-coordinating ligand for other organometallic compounds. In this paper, the utility of **2** in the formation of several new bi- and polymetallic complexes is demonstrated (Scheme I).

Experimental Section

All reactions were conducted under nitrogen using standard Schlenk type flask and cannula techniques. Workup procedures were done in air.

Elemental analyses were done at the Korea Basic Science Center. ^1H NMR spectra were obtained with either a Bruker AC 80 or Varian XL-200 instrument. Infrared spectra were recorded on a Perkin-Elmer 782 spectrometer or on a Bruker IFS 113 spectrometer (spectra measured as films on NaCl by evaporation of solvent).

$[(benzene)Mn(CO)_3]PF_6$, NaCp, $M(CO)_3(CH_3CN)_3$ (M = Cr, Mo, W), and $M(CO)_5Br$ (M = Mn, Re) were synthesized according to the published procedures.[3-5]

Synthesis of Compound 2. Excess NaCp (3 equiv) was added via syringe to a suspension of $[(benzene)Mn(CO)_3]PF_6$ (**1**; 1.00 g, 2.76 mmol) in 10 mL of THF at 0 °C under N_2. After 30 min, the reaction mixture was warmed to room temperature. The excess NaCp was destroyed by adding several drops of saturated aqueous NH_4Cl solution. The resulting solution was extracted with 30 mL of diethyl ether and distilled water, and then the organic layer was collected, dried ($MgSO_4$), and evaporated to yield a yellow residue. The yellow residue was chromatographed on silica gel with cyclohexane as eluant. The first band eluting was the product **2**. After evaporation of the solvent, the yield was 91% (0.71 g): mp 105 °C dec. IR (NaCl): ν_{CO} 2006, 1934, 1908 cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.35 (d, J = 5.37 Hz), 6.30 (d, J = 5.37 Hz), 6.28 (d, J = 5.37 Hz), 6.19 (d, J = 5.37 Hz), 5.91 (s), 5.78 (t, J = 5.13 Hz), 5.73 (s), 4.88 (t, J = 5.13 Hz), 3.56 (t, J = 5.61 Hz), 3.34 (t, J = 6.59 Hz), 2.83 (s), 2.67 (s) ppm. ^{13}C NMR ($CDCl_3$): δ 223.0, 154.9, 152.6, 134.4, 131.6, 131.3, 126.1, 125.3, 96.4, 96.1, 79.3, 79.2, 57.6, 56.6, 40.6, 40.1, 35.6, 34.8 ppm. Anal. Calcd for $C_{13}H_{11}MnO_3$: C, 59.59; H, 3.93. Found: C, 59.58; H, 3.77.

Synthesis of Compound 4. Compound **2** (0.34 g, 1.2 mmol) and 40 mL of benzene were placed in a Schlenk flask. *n*-BuLi (1.5 mmol, 0.6 mL of a 2.5 M solution in *n*-hexane) was added dropwise to the flask at room temperature. After being stirred for 1 h, the solution turned to a suspension. $BrMn(CO)_5$ (0.41 g, 1.5 mmol) was added to the reaction flask while being vigorously flushed with nitrogen gas, and the mixture was refluxed for 20 h. The reaction mixture was cooled to room temperature and filtered through anhydrous $MgSO_4$ in a fritted glass filter. Removal of the solvent gave yellow crude solids. The yellow solid was column-chromatographed on neutral alumina with cyclohexane. The first band eluting was unreacted compound **2**, and the second band eluting was compound **4a**. After evaporation of the second band, a 42% yield (0.22 g) of compound **4a** was obtained: mp 121 °C dec. IR (NaCl): ν_{CO} 2020, 1935, 1918, 1911 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.79 (t, J = 5.1 Hz, 1 H), 4.92 (t, J = 5.6 Hz, 2 H), 4.78 (s, Cp), 3.31 (m, 3 H) ppm. Anal. Calcd for $C_{17}H_{10}Mn_2O_6$: C, 48.60; H, 2.40. Found: C, 49.01; H, 2.03.

4b (yield 43%): mp 141 °C. IR (NaCl): ν_{CO} 2013, 2007, 1956, 1931, 1899 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.79 (t, J = 5.65 Hz, 1 H), 5.08 (m, Cp), 4.91 (J = 5.2 Hz, 2 H), 3.31 (m, 3 H) ppm. Anal. Calcd for $C_{17}H_{10}MnReO_6$: C, 37.03; H, 1.83. Found: C, 37.01; H, 1.76.

Synthesis of Compound 5. A typical procedure is as follows. Compound **2** (0.34 g, 1.2 mmol) and 10 mL of THF were placed in a Schlenk flask. *n*-BuLi (1.5 mmol, 0.6 mL of a 2.5 M solution in *n*-hexane) was added dropwise to the reaction flask at 0 °C. While it was stirred for 1 h, the solution turned to a deep yellow-brown. The resulting solution was transferred via cannula to another flask containing $Mo(CO)_3(CH_3CN)_3$ (0.69 g, 2.27 mmol, generated in situ and used without isolation) in 10 mL of THF. The reaction mixture was refluxed for 12 h and then cooled to room temperature. MeI was added to the resulting solution. The solution was stirred for 5 h, and the solvent was removed on a

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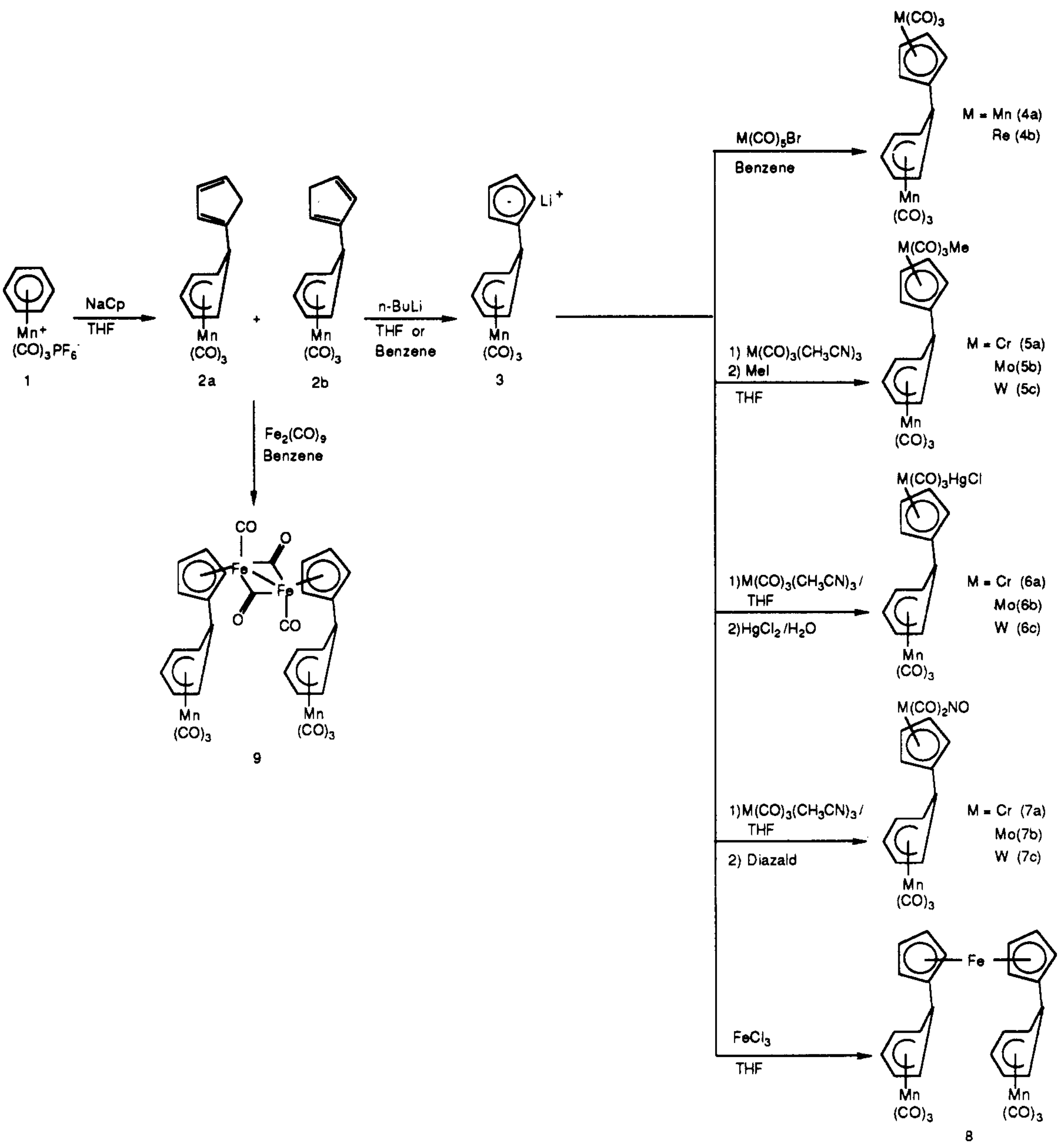
Scheme I



rotary evaporator. The resulting residue was extracted with diethyl ether. The ether extracts were evaporated to dryness. The yellow residue was column-chromatographed on neutral alumina with diethyl ether/hexane (1:10) under N_2. The yield of **5b** was 60%.

5b: mp 114 °C dec. IR (NaCl): ν_{CO} 2015, 1946, 1928, 1903 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.77 (t, J = 5.26 Hz, 1 H), 5.09 (t, J = 2.28 Hz, 2 H), 4.94 (t, J = 5.40 Hz, 2 H), 4.88 (t, J = 2.25 Hz, 2 H), 3.26 (m, 3 H), 0.31 (s, Me) ppm. Anal. Calcd for $C_{18}H_{13}MnMoO_6$: C, 45.40; H, 2.75. Found: C, 45.09; H, 2.30.

5c (yield 60%): mp 139 °C. IR (NaCl): ν_{CO} 2013, 1937, 1923, 1901 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.79 (t, J = 5.49 Hz, 1 H), 5.18 (t, J = 2.27 Hz, 2 H), 4.95 (t, J = 2.25 Hz, 2 H), 4.92 (t, J = 5.78 Hz, 2 H), 3.27 (m, 3 H), 0.37 (s, Me) ppm. Anal. Calcd for $C_{18}H_{13}MnO_6W$: C, 38.33; H, 2.32. Found: C, 38.08; H, 2.12.

Synthesis of Compound 6. A typical procedure is almost the same as the synthesis of compound **5**, except $HgCl_2$ is used instead of MeI.

6a (yield 45%): mp 182 °C dec. IR (NaCl): ν_{CO} 2019, 1986, 1920 (s, br) cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.83 (t, J = 5.4 Hz, 1 H), 4.99 (t, J = 5.1 Hz, 2 H), 4.83 (m, 4 H, Cp), 3.34–3.24 (m, 3 H) ppm.

6b (yield 72%): mp 82 °C dec. IR (NaCl): ν_{CO} 2007, 2000, 1911 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.80 (t, J = 5.37 Hz, 1 H), 5.24 (s, Cp, 4 H), 4.96 (t, J = 5.59 Hz, 2 H), 3.22 (m, 3 H) ppm. Anal. Calcd for $C_{17}H_{10}ClHgMnMoO_6$: C, 2924; H, 1.45. Found: C, 29.29; H, 1.51.

6c (yield 92%): mp 98 °C dec. IR (NaCl): ν_{CO} 2017, 2002, 1915 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.80 (t, J = 5.42 Hz, 1 H), 5.33 (m, Cp, 4 H), 4.98 (t, J = 5.35 Hz, 2 H), 3.25 (m, 3 H) ppm. Anal. Calcd for $C_{17}H_{10}ClHgMnO_6W$: C, 26.01; H, 1.28. Found: C, 25.56; H, 1.29.

Synthesis of Compound 7. A typical procedure is almost the same as the synthesis of compound **5**, except Diazald is used instead of MeI.

7a (yield 70%): mp 110 °C dec. IR (NaCl): ν_{CO} 2013, 1929 cm^{-1}; ν_{NO} 1688 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.79 (t, J = 5.37 Hz, 1 H), 4.95 (t, J = 5.60 Hz, 2 H), 4.80 (s, Cp), 3.32 (m, 3 H) ppm. Anal. Calcd for $C_{16}H_{10}CrMnNO_6$: C, 45.84; H, 2.40; N, 3.34. Found: C, 45.77; N, 2.02; N, 3.12.

7b (yield 70%): mp 110 °C dec. IR (NaCl): ν_{CO} 2011, 1927 cm^{-1}; ν_{NO} 1653 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.79 (t, J = 5.26 Hz, 1 H), 4.93 (t, J = 5.10 Hz, 2 H), 4.48 (s, Cp), 3.29 (m, 3 H) ppm. Anal. Calcd for $C_{16}H_{10}MnMoNO_6$: C, 41.49; H, 2.18; N, 3.02. Found: C, 41.28; H, 1.88; N, 2.66.

7c (yield 70%): mp 129 °C dec. IR (NaCl): ν_{CO} 2016, 2005, 1915 cm^{-1}; ν_{NO} 1646 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.80 (t, J = 5.31 Hz, 1 H), 5.37 (s, Cp), 4.94 (t, J = 5.23 Hz, 1 H), 3.32 (m, 3 H)

Table I. Crystal Parameters and Procedural Information for $(CH_3)(CO)_2W[\eta^5\text{-}C_5H_4\text{-}\{(\eta^5\text{-}C_6H_6)Mn(CO)_3\}]$

formula	$WMnO_6C_{18}H_{13}$
fw	564.085
space group	$P2_1/n$
a, Å	7.954 (1)
b, Å	21.932 (3)
c, Å	10.509 (1)
β, deg	96.40 (1)
V, Å^3	1822.0 (5)
Z	4
d(calcd), g cm^{-3}	2.056
cryst size, mm	0.13 × 0.33 × 0.40
μ, cm^{-1}	67.28
scan method	$\omega/2\theta$
data collected	$-h,k,l$; $3 < 2\theta < 44°$
total no. of observns	3496
no. of unique data $>3\sigma(I)$	2552
no. of params refined	248
abs cor factor range	0.6412–0.9990
GOF	0.700
$R = (\sum\|F_o - F_c\|)/\sum\|F_o\|$	0.0242
$R_w = (\sum\|F_o - F_c\|w^{1/2})/\sum\|F_o\|w^{1/2}$ [a]	0.0281

[a] $w = 1.00/(\sigma^2(F) + 0.002326F^2)$.

ppm. Anal. Calcd for $C_{16}H_{10}MnNO_6W$: C, 34.87; H, 1.83; N, 2.54. Found: C, 35.12; H, 1.78; N, 2.45.

Synthesis of Compound 8. While nitrogen gas was vigorously flushed through, anhydrous $FeCl_3$ (0.26 g, 1.6 mmol) was added to **3** (generated in situ) in THF (20 mL). The reaction mixture was refluxed for 24 h, cooled to room temperature, and filtered over anhydrous $MgSO_4$ in a fritted glass filter. The solution was evaporated to dryness, and the yellow residue was extracted with diethyl ether. The collected organic layer was washed with water successively (20 mL × 5), dried over $MgSO_4$, and evaporated to dryness. The residue was purified by column chromatography on neutral alumina with diethyl ether/hexane (1:10) as eluant. The yield was 52% (0.19 g): mp 188 °C dec. IR (NaCl): ν_{CO} 2008, 1932 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.75 (t + t′, 2 H), 4.85 (t + t′, 4 H), 3.95 (t, J = 1.82 Hz, 4 H), 3.75 (t, J = 1.82 Hz, 4 H), 3.33 (m, 6 H) ppm. Anal. Calcd for $C_{28}H_{20}FeMn_2O_6$: C, 54.40; H, 3.26. Found: C, 54.55; H, 2.98.

Synthesis of Compound 9. Excess $Fe_2(CO)_9$ was added to the benzene solution (20 mL) of compound **2** (0.42 g, 1.5 mmol) at room temperature. The reaction mixture was refluxed for 12 h. After the solution was cooled, any solids were filtered off. The filtrate was evaporated and the residue redissolved in THF. Compound **9** was obtained in 54% yield (0.32 g) by treating a THF solution with excess n-hexane: mp 217 °C dec. IR (NaCl): ν_{CO} 2013, 1979, 1919, 1760 cm^{-} ^1H NMR ($CDCl_3$): δ 5.80 (t, J = 5.3 Hz, 2 H), 4.95 (t, J = 5.6 Hz, 4 H), 4.43 (t, J = 2.1 Hz, 4 H), 4.23 (t, J = 2.1 Hz, 4 H), 3.65 (m, 1 H), 3.58 (m, 1 H), 3.51 (m, 2 H), 3.43 (m, 1 H), 3.36 (m, 1 H) ppm. Anal. Calcd for $C_{32}H_{20}Fe_2Mn_2O_{10}$: C, 48.90; H, 2.56. Found: C, 48.60; H, 2.84.

X-ray Data Collection, Structure Determination, and Refinement for Compound 5c. Crystals of **5c** were grown at room temperature from a methyl chloride solution of the compound. The crystal (0.13 × 0.33 × 0.40 mm) was mounted on an Enraf-Nonius CAD4 diffractometer, and the unit cell parameters were obtained from the least-squares fit of reflections (3° < 2θ < 44°). Data were collected with graphite-monochromated Mo Kα radiation by using the $\omega/2\theta$ scan mode. The crystal structure was solved by the use of the conventional heavy-atom method as well as Fourier difference techniques and refined by means of full-matrix least-squares procedures using SHELX-76.[6] All non-hydrogen atoms were refined by using anisotropic thermal factors, while most hydrogen atoms were located in a difference Fourier map and idealized with C–H = 1.08 Å. The last cycle of refinement converged with R = 2.42% and R_w = 2.81%. Crystal data, details of the data collection, and refinement parameters are listed in Table I. The final atomic parameters are given in Tables II and III.

Table II. Positional and Equivalent Isotropic Thermal Parameters for $(CH_3)(CO)_3W[\eta^5\text{-}C_5H_4\text{-}\{(\eta^5\text{-}C_6H_6)Mn(CO)_3\}]$

atom	x/a	y/b	z/c	U_{eq}, Å^2 [a]
W	0.1103 (<1)	0.2234 (<1)	1.0300 (<1)	0.034 (<1)
Mn	0.2522 (1)	0.0230 (<1)	0.6977 (1)	0.040 (1)
O(1)	0.6063 (7)	0.0150 (4)	0.8147 (6)	0.102 (7)
O(2)	0.3259 (9)	0.0529 (2)	0.4375 (5)	0.085 (5)
O(3)	0.2233 (10)	−0.1037 (2)	0.6065 (6)	0.102 (7)
O(4)	0.4798 (7)	0.2434 (4)	0.9645 (6)	0.102 (6)
O(5)	0.2077 (10)	0.3350 (3)	1.2061 (6)	0.107 (6)
O(6)	0.0710 (8)	0.2738 (3)	0.7515 (5)	0.080 (5)
C(1)	0.4693 (9)	0.0188 (4)	0.7651 (7)	0.065 (5)
C(2)	0.2989 (9)	0.0425 (3)	0.5400 (6)	0.052 (4)
C(3)	0.2362 (11)	−0.0545 (3)	0.6445 (7)	0.066 (6)
C(4)	0.3454 (9)	0.2370 (4)	0.9912 (6)	0.058 (5)
C(5)	0.1741 (10)	0.2941 (3)	1.1404 (7)	0.063 (5)
C(6)	0.0854 (8)	0.2549 (3)	0.8539 (6)	0.052 (4)
C(7)	−0.1188 (10)	0.2887 (4)	1.0117 (10)	0.070 (6)
C(11)	0.2417 (7)	0.1121 (2)	0.7933 (5)	0.038 (3)
C(12)	0.1054 (7)	0.1045 (3)	0.6981 (5)	0.043 (3)
C(13)	0.0015 (7)	0.0529 (3)	0.7031 (6)	0.048 (4)
C(14)	0.0415 (8)	0.0101 (3)	0.8023 (6)	0.049 (4)
C(15)	0.1784 (8)	0.0205 (2)	0.8951 (5)	0.043 (3)
C(16)	0.2367 (7)	0.0852 (2)	0.9235 (5)	0.036 (3)
C(21)	0.1310 (7)	0.1184 (2)	1.0130 (5)	0.037 (3)
C(22)	−0.0419 (7)	0.1337 (3)	0.9902 (6)	0.043 (3)
C(23)	−0.0956 (9)	0.1579 (3)	1.1026 (7)	0.056 (4)
C(24)	0.0461 (9)	0.1592 (3)	1.1972 (6)	0.054 (5)
C(25)	0.1844 (8)	0.1349 (3)	1.1432 (5)	0.046 (4)

[a] The equivalent isotropic U_{eq} is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Results and Discussion

$[(benzene)Mn(CO)_3]PF_6$ (**1**) reacts with NaCp in THF at 0 °C under N_2, to yield tricarbonyl(*exo*-cyclopentadienyl-η^5-cyclohexadienyl)manganese (**2**). Compound **2** is a mixture of two isomers having different positions of the double bonds on the cyclopentadiene rings. Both isomers almost equally exist.

Compound **2** can be easily lithiated in high efficiency by treating with n-BuLi. The lithiated compound, presumably **3**, was used without isolation. Refluxing **3** with $Mn(CO)_5Br$ in benzene produces the yellow compound **4a** in 42% yield, and refluxing with $Re(CO)_5Br$ produces the light yellow compound **4b** in 45% yield.[4] The yellow crystalline compounds **4a,b** are air-stable and soluble in organic solvents. The IR spectrum of **4a** reveals ν_{CO} absorptions of terminal CO ligands (2020, 2007 (sh), 1935, 1918, and 1911 cm^{-1}) attached to two different Mn atoms. The IR spectrum of **4b** displays metal carbonyl frequencies at 2013, 2007, 1956, 1936, and 1899 cm^{-1}. The IR spectrum for **2** exhibits three carbonyl stretching bands at 2006, 1934, and 1908 cm^{-1}. On the basis of intensity and position, the bands at 2020 and 1918 cm^{-1} are assigned to the carbonyl ligands of (cyclopentadienyl)$Mn(CO)_3$; the bands at 2013 and 1956 cm^{-1} belong to the carbonyl ligands of (cyclopentadienyl)$Re(CO)_3$. Compound **3** can be dinitrosylated by treating with $NOBF_4$.[7] The cyclopentadienyl ring of the lithiated compound **3** can be coordinated to a second metal (Mn or Re), demonstrating incorporation of two different transition metals into a single molecule.

Treatment of **3** with $M(CO)_3(CH_3CN)_3$ (M = Cr, Mo, W) and then with MeI led to the isolation of compounds **5a** (M = Cr), **5b** (M = Mo), and **5c** (M = W), respectively. The yellow compound **5a** was highly unstable and could not be characterized completely. However, the yellow compounds **5b,c** were stable under nitrogen. The ^1H NMR spectra for the methyl group of **5b,c** display singlet peaks at 0.31 and 0.37 ppm, respectively. The structure (Figure

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Table III. Bond Distances (Å) and Angles (deg) for $(CH_3)(CO)_3W[\eta^5\text{-}C_5H_4\text{-}\{(\eta^5\text{-}C_6H_6)Mn(CO)_3\}]$

W–C(4)	1.981 (7)	Mn–C(1)	1.794 (7)	O(2)–C(2)	1.145 (8)	C(14)–C(15)	1.397 (8)
W–C(5)	1.969 (7)	Mn–C(2)	1.791 (6)	O(3)–C(3)	1.153 (8)	C(15)--C(16)	1.513 (7)
W–C(6)	1.965 (6)	Mn–C(3)	1.788 (7)	O(4)–C(4)	1.144 (10)	C(16)–C(21)	1.516 (7)
W–C(7)	2.309 (7)	Mn–C(11)	2.204 (5)	O(5)–C(5)	1.145 (8)	C(21)–C(22)	1.410 (8)
W–C(21)	2.316 (5)	Mn–C(12)	2.135 (6)	O(6)–C(6)	1.147 (8)	C(21)–C(25)	1.433 (7)
W–C(22)	2.324 (5)	Mn–C(13)	2.107 (6)	C(11)–C(12)	1.401 (8)	C(22)–C(23)	1.404 (8)
W–C(23)	2.368 (6)	Mn–C(14)	2.123 (6)	C(11)–C(16)	1.495 (7)	C(23)–C(24)	1.417 (10)
W–C(24)	2.351 (6)	Mn–C(15)	2.219 (5)	C(12)–C(13)	1.405 (8)	C(24)–C(25)	1.399 (9)
W–C(25)	2.317 (6)	O(1)–C(1)	1.157 (8)	C(13)–C(14)	1.413 (9)		
C(5)–W–C(4)	79.3 (3)	C(24)–W–C(22)	58.4 (2)	C(14)–Mn–C(11)	79.0 (2)	C(15)–C(14)–Mn	75.0 (3)
C(6)–W–C(4)	75.6 (3)	C(24)–W–C(23)	35.0 (2)	C(14)–Mn–C(12)	69.3 (2)	C(15)–C(14)–C(13)	120.1 (5)
C(6)–W–C(5)	105.7 (3)	C(25)–W–C(4)	92.3 (3)	C(14)–Mn–C(13)	39.0 (2)	C(14)–C(15)–Mn	67.6 (3)
C(7)–W–C(4)	130.1 (3)	C(25)–W–C(5)	108.8 (3)	C(15)–Mn–C(1)	88.5 (3)	C(16)–C(15)–Mn	93.1 (3)
C(7)–W–C(5)	73.1 (3)	C(25)–W–C(6)	140.5 (3)	C(15)–Mn–C(2)	167.2 (2)	C(16)–C(15)–C(14)	119.2 (5)
C(7)–W–C(6)	73.0 (3)	C(25)–W–C(7)	135.7 (3)	C(15)–Mn–C(3)	104.6 (2)	C(15)–C(16)–C(11)	103.3 (4)
C(21)–W–C(4)	93.3 (3)	C(25)–W–C(21)	36.0 (2)	C(15)–Mn–C(11)	64.4 (2)	C(21)–C(16)–C(11)	116.8 (4)
C(21)–W–C(5)	144.3 (3)	C(25)–W–C(22)	58.7 (2)	C(15)–Mn–C(12)	79.5 (2)	C(21)–C(16)–C(15)	113.2 (4)
C(21)–W–C(6)	106.1 (2)	C(25)–W–C(23)	58.1 (2)	C(15)–Mn–C(13)	68.4 (2)	C(16)–C(21)–W	125.1 (3)
C(21)–W–C(7)	132.2 (3)	C(25)–W–C(24)	34.9 (2)	C(15)–Mn–C(14)	37.5 (2)	C(22)–C(21)–W	72.6 (3)
C(22)–W–C(4)	125.2 (3)	C(2)–Mn–C(1)	95.0 (3)	O(1)–C(1)–Mn	176.2 (7)	C(22)–C(21)–C(16)	127.4 (4)
C(22)–W–C(5)	150.2 (3)	C(3)–Mn–C(1)	96.2 (4)	O(2)–C(2)–Mn	177.3 (6)	C(25)–C(21)–W	72.0 (3)
C(22)–W–C(6)	97.6 (2)	C(3)–Mn–C(2)	87.3 (3)	O(3)–C(3)–Mn	177.7 (7)	C(25)–C(21)–C(16)	126.0 (5)
C(22)–W–C(7)	96.9 (3)	C(11)–Mn–C(1)	87.1 (3)	O(4)–C(4)–W	177.2 (7)	C(25)–C(21)–C(22)	106.4 (5)
C(22)–W–C(21)	35.4 (2)	C(11)–Mn–C(2)	103.4 (2)	O(5)–C(5)–W	178.3 (8)	C(21)–C(22)–W	72.0 (3)
C(23)–W–C(4)	149.4 (3)	C(11)–Mn–C(3)	168.5 (2)	O(6)–C(6)–W	179.4 (6)	C(23)–C(22)–W	74.3 (3)
C(23)–W–C(5)	115.5 (3)	C(12)–Mn–C(1)	123.0 (3)	C(12)–C(11)–Mn	68.5 (3)	C(23)–C(22)–C(21)	109.2 (5)
C(23)–W–C(6)	121.1 (3)	C(12)–Mn–C(2)	88.3 (3)	C(16)–C(11)–Mn	94.2 (3)	C(22)–C(23)–W	70.9 (3)
C(23)–W–C(7)	80.5 (3)	C(12)–Mn–C(3)	140.9 (3)	C(16)–C(11)–C(12)	120.6 (5)	C(24)–C(23)–W	71.9 (3)
C(23)–W–C(21)	58.6 (2)	C(12)–Mn–C(11)	37.6 (2)	C(11)–C(12)–Mn	73.9 (3)	C(24)–C(23)–C(22)	107.8 (6)
C(23)–W–C(22)	34.8 (2)	C(13)–Mn–C(1)	151.4 (3)	C(13)–C(12)–Mn	69.6 (3)	C(23)–C(24)–W	73.2 (3)
C(24)–W–C(4)	122.2 (3)	C(13)–Mn–C(2)	104.2 (3)	C(13)–C(12)–C(11)	118.8 (5)	C(25)–C(24)–W	71.3 (3)
C(24)–W–C(5)	95.4 (3)	C(13)–Mn–C(3)	105.6 (3)	C(12)–C(13)–Mn	71.8 (3)	C(25)–C(24)–C(23)	107.9 (5)
C(24)–W–C(6)	155.1 (2)	C(13)–Mn–C(11)	68.1 (2)	C(14)–C(13)–Mn	71.1 (4)	C(21)–C(25)–W	71.9 (3)
C(24)–W–C(7)	101.4 (3)	C(13)–Mn–C(12)	38.7 (2)	C(14)–C(13)–C(12)	118.5 (5)	C(24)–C(25)–W	73.9 (3)
C(24)–W–C(21)	59.1 (2)	C(14)–Mn–C(1)	124.7 (3)	C(13)–C(14)–Mn	69.9 (3)	C(24)–C(25)–C(21)	108.7 (6)
		C(14)–Mn–C(2)	140.2 (3)				
		C(14)–Mn–C(3)	90.1 (3)				

1) of **5c** obtained by the spectroscopic and X-ray crystallographic studies indicates that the methyltricarbonyl(η^5-cyclopentadienyl)tungsten moiety is positioned exo, as expected. The dienyl carbon atoms C(11), C(12), C(13), C(14), and C(15) define a nearly perfect plane with a deviation of 0.009 (1) Å. The cyclohexadienyl ring is folded about C(11)–C(15) with an angle of 39.6°. The plane through C(13)–C(16)–C(21) nearly coincides with the cyclopentadienyl ring (dihedral angle 8.6°). The manganese atom is located 1.667 Å below the plane of the dienyl ring. The coordination sphere around tungsten can be viewed as a pseudo square pyramid with three carbonyls (mean W–C = 1.971 Å, C–O = 1.145 Å) and the CH_3 group (W–C = 2.309 (7) Å) forming the base. The tungsten atom is located 2.002 Å below the plane of the cyclopentadienyl ring.

Treatment of **3** with $M(CO)_3(CH_3CN)_3$ (M = Cr, Mo, W) and then with $HgCl_2$ led to the isolated compounds **6a** (M = Cr), **6b** (M = Mo), and **6c** (M = W), respectively. In the beginning, we expected that M–Hg–M type compounds would be obtained.[8] However, trinuclear complexes (**6**) containing a M–Hg–Cl structural unit were isolated. Thus, M–Hg–X (where M = Cr, Mo, W) complexes[9] have now been prepared by a facile, high-yield synthesis. Although the reaction appears to be the same as that used to prepare M–Hg–M,[8] our reactions provide no evidence for the formation of M–Hg–M. Compounds **6b**,**c** are air-stable yellow crystalline solids, but they are air-sensitive when dissolved in polar organic solvents. The greenish yellow compound **6a** is air-stable in the solid state but quite unstable in polar organic solvents. These M–Hg–X compounds can be used to make M–Hg–M′–X type compounds.[10]

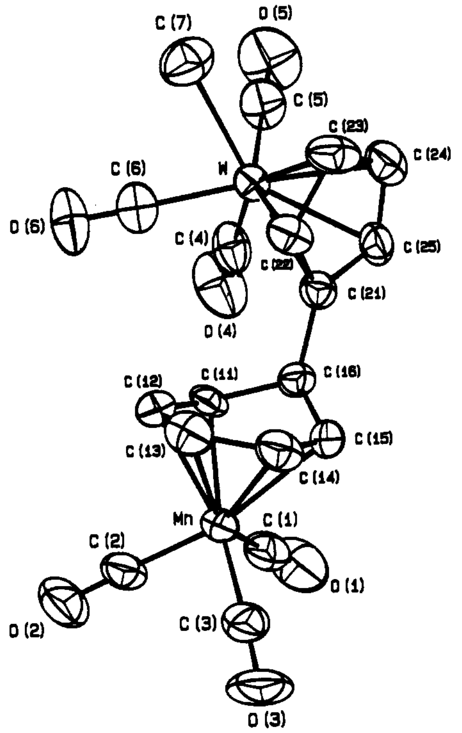

Figure 1. ORTEP drawing of tricarbonyl[[methyltricarbonyl(η^5-cyclopentadienyl)tungsten)-η^5-cyclohexadienyl]manganese (**5c**).

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Treatment of **3** with $M(CO)_3(CH_3CN)_3$ (M = Cr, Mo, W) and then with Diazald led to the isolated compounds **7a** (M = Cr), **7b** (M = Mo), and **7c** (M = W), respectively, in high yields. When the nitrosylation was performed by using $NOBF_4$, the yields were rather low. The red-orange chloroform solutions of compounds **7** were stable enough to record their IR and ^1H NMR spectra. The IR spectra of nitrosyl ligands in compounds **7a–c** display absorption frequencies at 1689, 1653, and 1646 cm^{-1}. As in the case of other cyclopentadienyl compounds, the stretching frequencies of nitrosyl ligands decrease as the central metal becomes heavier.[11] Compounds **7** are quite stable under N_2 and soluble in most organic solvents. This reaction demonstrates the incorporation of two transition metals (Mn and chromium triad metals) in a single molecule.

Treatment of **3** with $FeCl_3$ led to the isolation of compound **8**, a heterometallic derivative of ferrocene.[12] The orange crystalline compound **8** is air-stable and thermally decomposed at ca. 188 °C. The ^1H NMR spectrum of **8** in $CDCl_3$ shows the typical pattern for a 1,1′-disubstituted ferrocene system[13] and peaks typical of cyclohexadienyl ring protons. Two slightly deshielded triplets at δ 3.95 (t, J = 1.82 Hz) and 3.75 (t, J = 1.82 Hz) are observed for the cyclopentadienyl ring protons. This reaction demonstrates the incorporation of three transition metals in a single molecule.

Treatment of **2** with $Fe_2(CO)_9$ led to the isolation of compound **9**. Compound **9** is air-stable and thermally decomposed at ca. 217 °C. The IR spectrum of **9** displays a bridging carbonyl frequency at 1760 cm^{-1}. Compound **9** might be used as a useful precursor to a variety of substituted cyclopentadienyliron compounds. This reaction demonstrates the incorporation of four transition metals in a single molecule.

It has been demonstrated that exploring the use of compound **2** or the lithiated compound **3** as a π-coordinating ligand is a synthetically valuable procedure. With the appropriate organometallic reagents, bi- or polynuclear compounds can be easily obtained in reasonable yield.

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Registry No. 1, 38834-51-4; **2a**, 142159-64-6; **2b**, 142159-65-7; **4a**, 142159-66-8; **4b**, 142159-67-9; **5a**, 142159-68-0; **5b**, 142159-69-1; **5c**, 142159-70-4; **6a**, 142159-71-5; **6b**, 142159-72-6; **6c**, 142159-73-7; **7a**, 142159-74-8; **7b**, 142159-75-9; **7c**, 142159-76-0; 8, 142159-77-1; **9**, 142159-78-2; $BrMn(CO)_5$, 14516-54-2; $BrRe(CO)_5$, 14220-21-4; $Cr(CO)_3(CH_3CN)_3$, 16800-46-7; $Mo(CO)_3(CH_3CN)_3$, 15038-48-9; $W(CO)_3(CH_3CN)_3$, 16800-47-8; $FeCl_3$, 7705-08-0; $HgCl_2$, 7487-94-7; $Fe_2(CO)_9$, 15321-51-4.

Supplementary Material Available: Tables of anisotropic thermal parameters for the non-hydrogen atoms and positional and isotropic thermal parameters for the hydrogen atoms of **5c** (2 pages). Ordering information is given on any current masthead page.

OM920091B

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Effect of an N–N Chelate Ligand on the Insertion Reactions of Carbon Monoxide into a Manganese–Alkyl Bond

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The reduction of *fac*-$[Mn(N{-}N)(CO)_3Br]$ {N–N = 2,2′-bipyridine, bpy, **1a**; 1,10-phenanthroline, phen, **1b**; 1,4-di-*tert*-butyl-1,4-diaza-1,3-butadiene, ^tBu-DAB, **1c**} with sodium amalgam followed by the addition of MeI affords the methyl tricarbonyl derivatives *fac*-$[Mn(N{-}N)(CO)_3Me]$ (N–N = bpy, **2a**; phen, **2b**; ^tBu-DAB, **2c**). Complexes of type **2** react with two-electron donor ligands L to yield the acyl complexes *cis,trans*-$[Mn(N{-}N)(CO)_2(L)(COMe)]$ {N–N = bpy: L = CO, **3a**; CN-^tBu, **3b**; CN-2,6-dimethylphenyl (CN-2,6-Xyl), **3c**; $P(OMe)_3$, **3d**; PEt_3, **3e**. N–N = phen: L = CO, **3f**; CN-^tBu, **3g**. N–N = ^tBu-DAB: L = CO, **3h**; CN-^tBu, **3i**}. The reaction of *fac*-$[Mn(bpy)(CO)_3Me]$ (**2a**) with *CO (CO 99% enriched in ^{13}C) affords *cis,trans*-$[Mn(bpy)(CO)_2(^*CO)(COMe)]$ (**4**), ruling out the formation of any intermediate $[Mn(bpy)(CO)_2(^*CO)(COMe)]$ (**5a–c**), in which the acyl and the *CO ligands were mutually cis and, therefore, supporting the hypothesis that the incoming ligands enter trans to the acyl group in the formation of complexes of type **3**. The structure of *cis,trans*-$[Mn(phen)(CO)_2(CN\text{-}^tBu)(COMe)]$ (**3g**) has been determined by X-ray diffraction methods. M = 417.3, orthorhombic, space group $Pn2_1a$ ($Pna2_1$ standard), a = 21.146 (8), b = 10.464 (5), c = 9.183 (5) Å, V = 2032 (2) Å^3, Z = 4, D_c = 1.36 g cm^{-3}. Mo Kα radiation (graphite crystal monochromator, λ = 0.71073 Å), μ = 6.5 cm^{-1}, $F(000)$ = 864, T = 293 K. Final conventional R factor 0.062 for 731 "observed" reflections and 148 parameters.

Introduction

The insertion of carbon monoxide into metal–alkyl bond has been extensively investigated, as acyl complexes are involved in many catalytic and stoichiometric carbonylation and decarbonylation reactions, both in the laboratory and in industry.[1] Thus, the stereochemistry at the metal

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